Electronic Supplementary Information for Dalton Transactions

Supporting Information for

U(IV) and U(V) azide complexes supported by amide or aryloxide ligands.

Skye Fortier, Guang Wu, Trevor W. Hayton*

Department of Chemistry & Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106

Experimental

Caution! All covalent azides should be handled with extreme care as they can detonate unexpectedly due to friction or shock.

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under a high vacuum or an atmosphere of argon or nitrogen. Diethyl ether, hexanes, and THF were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system. All deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and were dried over activated 4 Å molecular sieves for 24h prior to use. $[Li(THF)]_2[U(O^tBu)_6]$,[1] $UCl[N(SiMe_3)_2]_3$,[2] and $U[N(SiMe_3)_2]_3$[3] were synthesized according to published procedures. All other reagents were obtained from commercial sources and used as received.

NMR spectra were recorded on a Varian UNITY INOVA 400 or a Varian UNITY INOVA 500 spectrometer. ^1H NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (^1H NMR experiments). $^7Li\{^1H\}$ NMR spectra are referenced to external saturated solution of LiCl in deuterium oxide. IR spectra were recorded on a Mattson Genesis FTIR spectrometer. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

$[Li(THF)_3]_2[U(O\text{-}2,6\text{-}Me_2C_6H_3)_4(N_3)_2]$ (1). To a stirring solution of $[Li(THF)]_2[U(O^tBu)_6]$ (0.075 g, 0.090 mmol) in THF (4 mL) was added a THF (1 mL) solution of 2,6-$Me_2C_6H_3OH$ (0.066 g, 0.540 mmol) and Me_3SiN_3 (0.026 ml, 0.197 mmol). Upon addition, the solution immediately turned green. After stirring for 2 h, the solvent was removed in vacuo to yield an amber oil. The oil was washed with hexanes (2 × 4 mL) which resulted in the formation of a white solid. The solid was dissolved in a mixture of Et_2O (3 mL) and THF (2 mL) affording an amber solution. The solution was layered with hexanes (5 mL) and stored at -25 °C for 12 h, resulting in the deposition of pale green crystals. The solid was washed with hexanes (3 × 4 mL) and dried under vacuum. Upon standing, the crystals turned opaque in colour. 0.084 g, 74% yield. Note that the addition of excess Me_3SiN_3 to the reaction only results in the formation of an intractable mixture. ^{1}H NMR (400 MHz, 22 °C, C_6D_6): δ -3.75 (br s, 48H, THF), 8.86 (s, 24H, Me), 12.26 (s, 4H, para CH), 14.12 (s, 8H, meta H). ^{7}Li{^{1}H} NMR (194 MHz, 22 ºC, C_6D_6): No signal observed. Anal Calcd for $C_{56}H_{84}Li_2N_6O_{10}U$: C, 53.67; H, 6.77; N, 6.71. Found: C, 50.66; H, 6.17; N, 7.07. Anal Calcd for $[Li(THF)_2]_2[U(O\text{-}2,6\text{-}Me_2C_6H_3)_4(N_3)_2]$, $C_{48}H_{68}Li_2N_6O_8U$: C, 51.98; H, 6.19; N, 7.58. Found: C, 50.66; H, 6.17; N, 7.07.

$\{[Na(THF)_4][U[N(SiMe_3)_2]_3(N_3)_2]\}_x$ (2). To a solution of $UCl[N(SiMe_3)_2]_3$ (0.677 g, 0.897 mmol) in THF (8 mL) was added NaN_3 (0.553 g, 8.509 mmol). The mixture was stirred for 24 h resulting in an opaque, pink suspension. The resulting suspension was filtered through a Celite column (3 cm × 2 cm) supported on a glass frit, and the filtrate volume was reduced in vacuo to 2 mL. The pink solution was layered with hexanes (10 mL) and stored at -25 °C for 12 h, resulting in the deposition of pink crystals. 0.538 g, 54% yield. Crystals of **2** turned opaque and faint pink upon application of vacuum. ^{1}H NMR (400 MHz, 22 °C, C_6D_6/CD_2Cl_2): δ -4.25 (br s, 54H, $SiMe_3$), 1.43 (s, 24H, α-THF protons), 3.61 (s, 24H, β-THF protons). Anal Calcd for $[Na(THF)_4][U[N(SiMe_3)_2]_3(N_3)_2]$, $C_{34}H_{86}N_9NaO_4Si_6U$: C, 36.6; H, 4.89; N, 11.3. Found: C, 31.21; H, 7.26; N, 12.17. Anal Calcd for $[Na(THF)_2][U[N(SiMe_3)_2]_3(N_3)_2]$, $C_{26}H_{70}O_2N_9NaSi_6U$: C, 32.18; H, 7.29; N, 12.99. Found: C, 31.21; H, 7.26; N, 12.17.

$[Li(THF)_3][U(O\text{-}2,6\text{-}C_6H_3)_5(N_3)]$ (3). To a solution of **1** (0.010 g, 0.008 mmol) in THF (2 mL) was added AgCl (0.003 g, 0.021 mmol). The solution immediately turned dark red and gas evolution was observed. After 10 minutes, gas evolution ceased and the solution was filtered through a Celite column (2 cm × 2 cm) supported on a glass frit. The filtrate was layered with hexanes (5 mL) and stored at -25 °C for 12 h, resulting in the deposition of an unidentified red oil. The supernatant was then decanted into a new vial, the volume reduced by half in vacuo, and the vial was stored at -25 °C for 12 h, resulting in the deposition of red crystals. The crystals were washed with hexanes (2 × 1 mL) and dried under vacuum to afford 1.2 mg of solid. ^{1}H NMR (400 MHz, 22 °C, C_6D_6): δ 1.40 (s, 12H, α-THF protons), 2.11 (s, 6H, Me), 3.13 (s, 24H, Me), 3.57 (s, 12H, β-THF), 5.33 (s, 1H, para H), 5.64 (s, 4H, para H), 7.68 (s, 2H, meta H), 8.32 (s, 8H, meta H).

$U[N(SiMe_3)_2]_3(N_3)_2$ (4). To a pale pink suspension of **2** (0.153 g, 0.137 mmol) in Et_2O (4 mL) was added AgOTf (0.035 g, 0.137 mmol). After stirring for 2 h, the solvent was removed in vacuo yielding a dark red solid. The solid was dissolved in hexanes (4 mL) and filtered through a Celite column (3 cm × 2 cm) affording a red filtrate. The filtrate volume was reduced in vacuo to 1 mL and the vial was stored at -25 °C for 24 h resulting in the deposition of dark red crystals. 0.064 g, 58% yield. ^{1}H NMR (500 MHz, 22 °C, C_6D_6): δ -1.65 (br s, 54H, Me). Anal Calcd for $C_{18}H_{54}N_9Si_6U$: C, 26.91; H, 6.78; N, 15.69. Found: C, 26.77; H, 6.63; N, 15.43.

$U[N(SiMe_3)_2]_3(N_3)_2$ (5). To a stirring solution of **4** (0.023 g, 0.028 mmol) in hexanes (2 mL) was added a hexanes (2 mL) solution of $U[N(SiMe_3)_2]_3$ (0.020 g, 0.028 mmol). Upon addition, the solution immediately turned orange. After 1 h, the solution volume was reduced to 2 mL in vacuo. Storage of the solution at -25 °C for 24 h resulted in the deposition of orange crystals. 0.022 g, 52% yield. ^{1}H NMR (400 MHz, 22 °C, C_6D_6): δ -3.70 (br s, 54 H, Me). IR (KBr pellet, cm^{-1}): 2962 (m), 2902 (w), 2105 (s), 2082 (s), 1384 (w), 1362 (2), 1249 (s), 1186 (w), 1076 (w), 910 (s), 850 (s), 773 (m), 685 (m), 617 (m). This complex has been previously prepared.[4]

X-ray Crystallography. Data for **1**, **2**, **3**, and **4**·C_6H_{14} were collected on a Bruker 3-axis platform diffractometer equipped with a SMART-1000 CCD detector using a graphite monochromater with a Mo K α X-ray source (α = 0.71073 Å). The crystals were mounted on a glass fibre under Paratone-N oil and all data collected at 150(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans with 0.3° frame widths. Frame exposures of 10, 10, 30 and 20 seconds were used for complexes **1**, **2**, **3**, and **4**·C_6H_{14}, respectively. Data collection and cell parameter determination were conducted using the SMART program.[5] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[6] Absorption correction of the data was carried out empirically based on reflection ψ-scans. Subsequent calculations were carried out using SHELXTL.[7] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment with exceptions noted in the subsequent paragraph. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[7]

One coordinated THF molecule in **1** was disordered and was subsequently modeled over two positions with refined occupancies of 0.58 and 0.42. Idealized hydrogens were not assigned to the disordered atoms. For **2**, the THF molecules were disordered. The disorder was addressed by applying restraints (ISOR, DELU, SIMU) and fixing the C-C bond lengths to 1.50(1) Å. The O-C distances of the disordered THF molecules were fixed to 1.40(1) Å.

A summary of relevant crystallographic data for **3**, **4**·C_6H_{14}, **6**, **7**, and **9** is presented in Table S1.

Table S1. X-ray Crystallographic Data for Complexes **1**, **2**, **3**, and **4**$\cdot C_6H_{14}$.

	1	**2**	**3**	**4**$\cdot C_6H_{14}$
Empirical formula	$C_{56}H_{84}Li_2N_6O_{10}U$	$C_{34}H_{86}N_9NaO_2Si_6U$	$C_{52}H_{69}LiN_3O_8U$	$C_{24}H_{68}N_9Si_6U\cdot C_6H_{14}$
Crystal Habit, color	block, clear	rod, pink	plate, dark red	block, dark red
Crystal size (mm)	0.8 x 0.4 x 0.3	0.55 x 0.35 x 0.35	0.4 x 0.16 x 0.05	0.5 x 0.4 x 0.3
Crystal system	monoclinic	monoclinic	orthorhombic	Monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_12_12_1$	$C2/c$
Volume (Å^3)	2959.9(4)	5637.8(7)	5170(1)	4323.7(4)
a (Å)	11.4965(8)	19.425(1)	12.525(1)	18.767(1)
b (Å)	22.525(2)	11.8336(8)	20.098(2)	14.6497(8)
c (Å)	12.6040(9)	25.319(2)	20.536(2)	16.8791(9)
α(°)	90	90	90	90
β(°)	114.922(2)	104.369(2)	90	111.295(2)
γ(°)	90	90	90	90
Z	2	4	4	4
Formula weight (g/mol)	1253.20	1114.68	1109.07	889.44
Density (calculated) (Mg/m^3)	1.406	1.313	1.425	1.366
Absorption coefficient (mm^{-1})	2.800	3.053	3.193	3.946
F_{000}	1280	2288	2244	1804
Total no. reflections	23433	23319	42047	17620
Unique reflections	6184	5716	11085	4513
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0438$, $wR_2 = 0.1107$	$R_1 = 0.0483$, $wR_2 = 0.1209$	$R_1 = 0.0538$, $wR_2 = 0.1079$	$R_1 = 0.0243$, $wR_2 = 0.0561$
Largest diff. peak and hole (e$^-$Å^{-3})	4.342 and -1.796	2.781 and -1.811	2.252 and -1.478	1.540 and -0.454
GOF	0.904	1.009	0.940	1.011

References

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